U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP953

Part of Journal of Research of the National Bureau of Standards, Volume 17, December 1936

EXTRACTION, WITH ACETONE, OF SUBSTANTIALLY CONSTANT-BOILING FRACTIONS OF A "WATER-WHITE" LUBRICATING OIL[1]

By Beveridge J. Mair and Sylvester T. Schicktanz[2]

ABSTRACT

This paper describes the separation, with respect to type of molecule, effected by solvent extraction of substantially constant-boiling fractions of a "water-white" lubricating oil. Each charge of about 500 g was separated, by extraction in 14-m columns, into from 25 to 35 fractions. Kinematic viscosities at 100 and 210° F and refractive indices were determined on all fractions. In addition to the properties mentioned, carbon-hydrogen ratios, molecular weights, densities, dispersions, optical activities, boiling points, and aniline points were determined on about 30 "key" fractions. The extractor columns and their mode of operation are described.

CONTENTS

I. INTRODUCTION

This paper presents a continuation of the work on the chemical constitution of lubricating oil, undertaken at the National Bureau of Standards as part of the American Petroleum Institute Research Project 6. In particular, it describes the separation, with respect to type of molecules, effected by solvent extraction of oil which had previously been extensively distilled and which was substantially constant boiling. A correlation of the physical properties of certain fractions from this extraction process and their comparison with those of synthetic hydrocarbons of high molecular weight follows in a subsequent paper.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum. This paper was originally presented before the American Chemical Society at the Pittsburgh meeting in September 1936.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

II. PRELIMINARY TREATMENT OF THE LUBRICANT FRACTION AND SCOPE OF THE PRESENT WORK

The preliminary treatment of the lubricant fraction of the mid-continent petroleum used in this work has been described previously [1] [3] and is illustrated graphically in figure 1. It consisted in separating the lubricant fraction by successive treatments into three parts: (1) An extract portion by extraction with sulphur dioxide; (2) a wax portion by crystallization from ethylene chloride at −18° C; and (3) a "water-white" oil portion by filtration through silica gel. This paper deals with the water-white portion only, the investigation of which was begun by distilling it under high vacuum with the object of separating it into fractions differing in molecular weight. The light and heavy ends from this distillation were placed in storage as indicated in figure 1, and distillation of the remainder was continued until substantially constant-boiling fractions were obtained. Charges were prepared for extraction by mixing according to their viscosities, the distillation fractions of about 45 g each. The weight of these charges and the approximate range in kinematic viscosity at 100° F and refractive index at 25° C of the fractions which it was necessary to mix to prepare each charge are shown in figure 1 under *Charges for Extraction*. Each charge was separated into from 25 to 35 fractions by extraction with acetone in 14-m columns. Kinematic viscosities at 100 and 210° F and refractive indices at 25° C were determined on all fractions from the extractors. However, these properties are reported only for the series designated in figure 1 as *A*, *B*, *C*, *D*, *E* and *F*, which were regarded as typical. In addition for the same series, carbon-hydrogen ratios, molecular weights, densities, dispersions, optical activities, boiling points, and aniline points were determined on certain "key" fractions.

III. DISTILLATION

The systematic distillation under high vacuum of the water-white oil was continued, using the equipment and procedure described previously [1]. When the range in viscosities of the fractions resulting from the distillation of each charge, particularly for the more volatile portions, finally became nearly as small as the range in viscosity of the fractions which were blended to make up a charge, it was decided that it was unprofitable to continue the distillation further. In figure 2 are plotted the viscosities of fractions resulting from the final distillation with respect to the percentage by weight of the charge. Curves for all the charges are not included, but those given are typical. On the right-hand side of the figure are indicated the weights of the individual charges, together with the range in viscosities of the fractions which it was necessary to mix to prepare a charge. Curves *I* to *V* are the result of seven distillations in short fractionating columns, while curves *VII* to *X* represent the result of four distillations in a column molecular still, followed by from four to seven distillations in simple molecular stills. Curve *VI* is the result of eight stages of molecular distillation followed by one distillation in a short fractionating column. There was of course an interchange between the two types of distillation, the more volatile

[3] The figures given in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.

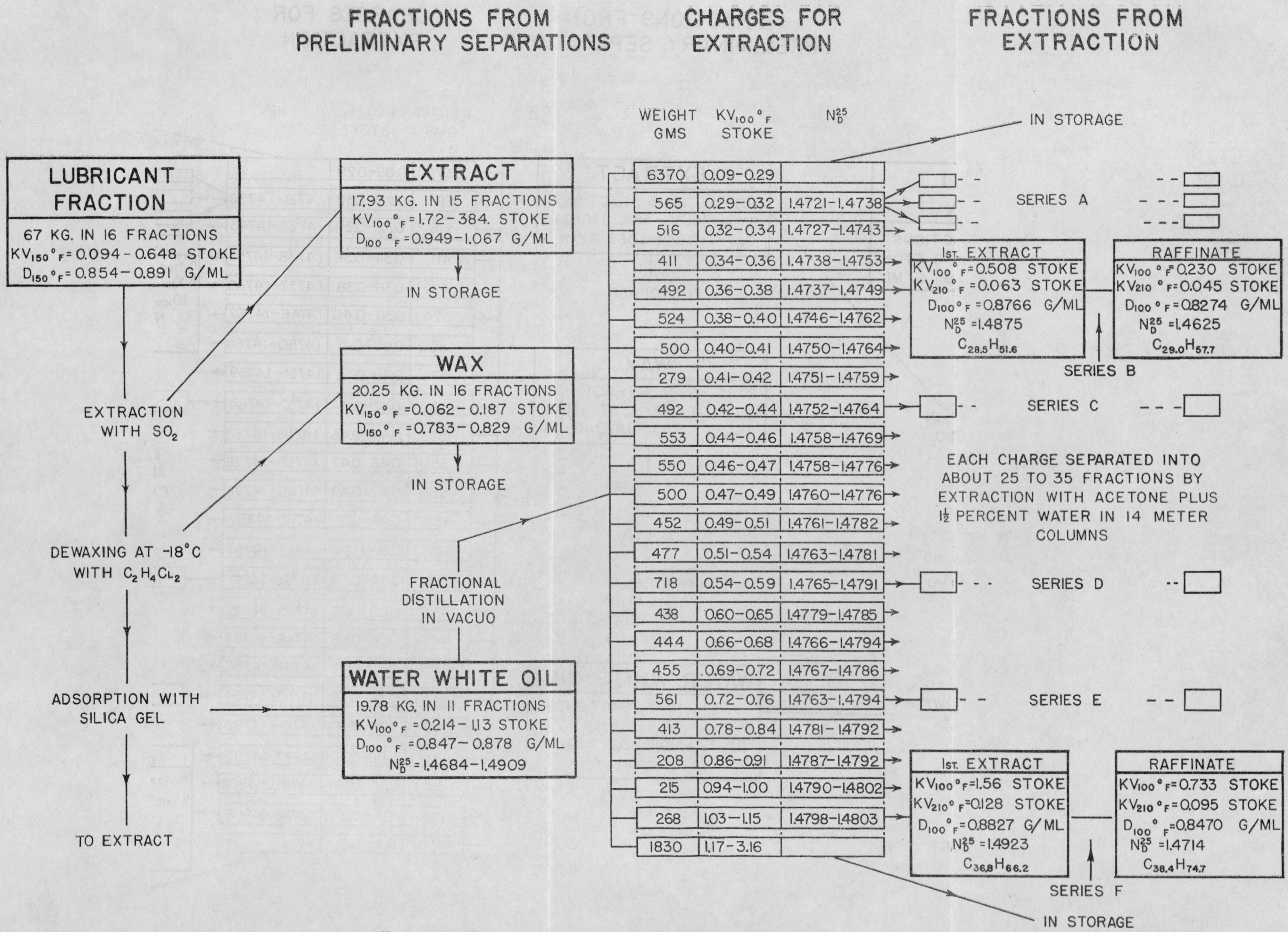

FIGURE 1.—*Chart showing treatment and disposition of lubricating oil fractions.*

106351—36 (Face p. 910)

fractions from the molecular stills (below 0.60 stoke) being charged for the next distillation into the fractionating columns, while the less volatile fractions from the fractionating columns (above 0.60 stoke) were charged into the molecular stills.

A greater range in the viscosity of the fractions from the distillation of the less volatile charges is noticeable. This may be due in part to the limited quantity of oil in this region, it being necessary

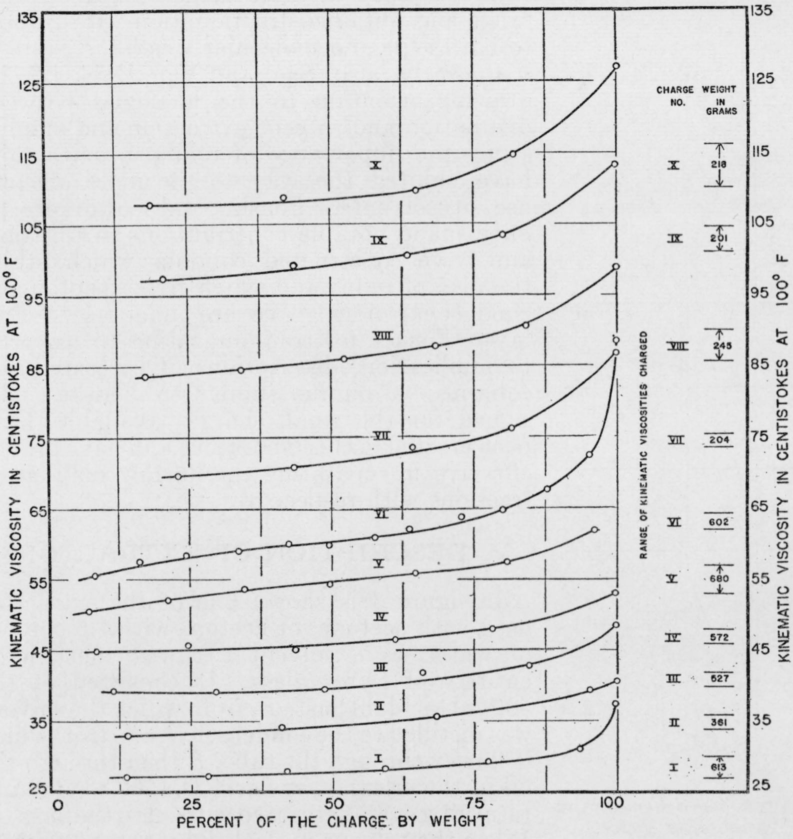

FIGURE 2.—*Viscosities of fractions from the final distillation.*

Each point represents by its ordinate the viscosity of a fraction, by its abscissa the percentage which had been distilled, including the fraction.

to blend fractions with a fairly wide range in viscosity to prepare even a small charge.

At the end of this systematic distillation, the oil originally water-white was somewhat colored, the distillates being pale yellow, while the still-pot residues were reddish brown.

IV. EXTRACTION WITH SOLVENTS

A powerful tool for investigating the composition of lubricating-oil fractions is now available in extraction with solvents. Solvents have been used for many years to effect a separation of the various

types of hydrocarbons in petroleum. It is only recently, however, that the twofold action of solvents in separating both with respect to molecular weight and with respect to type has been clearly recognized. It is evidently of importance to extract fractions composed of hydrocarbons with a narrow range of molecular weights if the maximum separation with respect to type is to be obtained. Consequently, the extraction experiments of the earlier investigators were not particularly successful, since they used fractions of wide boiling range and obtained fractionation with respect to both type and molecular weight.

Recently, also, Saal and Van Dyck [2], by drawing attention to the analogies between distillation and solvent extraction and emphasizing the importance of reflux in extraction, have pointed the way to the more efficient use of solvents. Fenske and coworkers [3] have made notable contributions in this field and have constructed columns which utilize the idea of reflux and which give exceptionally good separations. We are indebted to Professor Fenske for communicating to us, prior to publication, descriptions of his extraction columns. Columns similar to Fenske's, designed for the small charges available, have been erected in this laboratory and have proved effective in separating the narrow distillation fractions with respect to type.

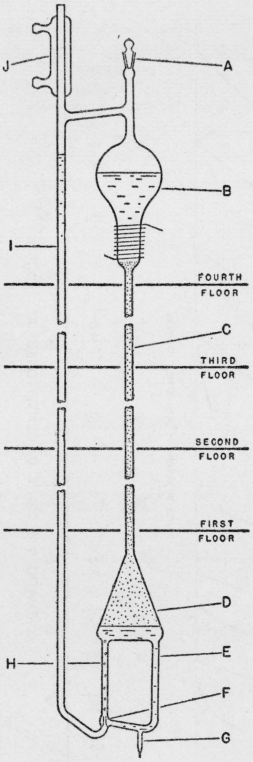

FIGURE 3.—*Schematic diagram of extractor.*

V. DESCRIPTION OF EXTRACTORS

In figure 3 is shown one of the extractors used with acetone, or acetone with 1.5 percent of water, as a solvent. It was constructed entirely of Pyrex glass. It consisted of the 500-ml kjeldahl flask, *B*, from which the solvent was distilled to the condenser, *J*, and from which it flowed through the tube, *I*, then through the oil in the erlenmeyer flask, *D*, (500 to 700 ml), returning again saturated with oil to the flask, *B*. When the solvent in flask *B* became saturated, oil came out of solution in the form of small globules, which, being heavier than the solvent, sank slowly to flask *D* against the ascending stream of solvent saturated with oil. The solvent entered the oil in the form of globules through the injector, *F*, and carried upward with it a stream of oil into flask *D*. This caused a circulation of oil through the system *H*, *D*, *E*, and insured thorough mixing of the oil and intimate contact with the solvent. The tubes *E* and *H* extended 30 cm below flask *D*. Distillation of the solvent was accomplished by electrical heating, the lower portion of the kjeldahl flask, *B*, being surrounded with an asbestos-insulated heating coil. To maintain smooth boiling the lower portion of the inside of flask *B* was coated with carborundum. *A* is a ground-glass joint, through which the

charge of oil and the solvent were introduced, and through which the individual fractions of acetone saturated with oil were withdrawn. *G* is a fine glass tip, which was broken when it was necessary to withdraw the oil residue and solvent left at the end of an experiment.

The desirability of obtaining a maximum separation of the comparatively small charges of oil (about 500 g) governed the choice of the dimensions of these extractor columns. It was important that the path where the counterflow of saturated acetone and oil globules occurred be as long as possible, and also that the "hold-up"; i. e., the amount of oil in solution and in the form of globules, in the column, represent a small fraction of the charge. For these reasons very tall extractor tubes with very small diameters were chosen. The extractors were located in an elevator shaft and extended from the basement to the fourth floor, a distance of about 14 m (C, fig. 3). Extractors with tubes 8, 6, and 4 mm in internal diameter were constructed. The 4-mm tubes, however, proved impractical since they clogged frequently with oil.

VI. CHOICE OF SOLVENT

Acetone, or acetone containing 1.5 percent of water, which was thought to be slightly more selective than pure acetone, was selected as a solvent. Many highly selective solvents—i. e., those solvents which give a good separation with respect to type—have been reported. Most of these, however, boil at elevated temperatures and were thought likely to be difficult to remove completely from the oil, and also likely to attack the oil at the temperatures necessary to distil and circulate them in the type of column just described. Methyl cyanide, one of the lower boiling solvents, was tried, but the globules of oil instead of falling freely stuck to the glass tubing, eventually clogging the column.

VII. OPERATION OF EXTRACTOR COLUMNS

After the circulation of acetone had commenced, about 6 hours were required before the acetone in flask *B* was saturated and oil globules appeared. Two more hours were required before these globules traveled 14 m to the flask at the bottom of the column. After a suitable interval of time (16 to 32 hours) necessary for the attainment of equilibrium had elapsed, a fraction of acetone saturated with oil was withdrawn, and fresh acetone was added through the top of the condenser. This procedure was continued until all but a small residue of oil had been removed as fractions in solution in acetone. The greater part of the acetone was distilled off from the oil fractions, while the last traces were removed by sweeping out with carbon dioxide for 12 hours at 100° C. The residue in the column, removed by breaking tip *G*, was freed from acetone in a similar manner. Fractions of about 15 g, the amount required for determining physical properties, were obtained. The size of these fractions depended on the solubility of oil in acetone, and could be controlled to some extent by varying the quantity of acetone (200 to 350 ml) in flask *B*. It can be seen that this mode of operating is analogous to fractional distillation under total reflux. The oil container, *D*, corresponds to

the still pot, the flask, *B*, to the reflux condenser and receiver, while the column itself is analogous to the column in fractional distillation. The oil in solution corresponds to the vapor phase in distillation while the oil globules correspond to the liquid reflux.

An enlargement of a photograph of a small section of an extractor column is shown in figure 4. The small size of the oil globules is apparent by comparing them with the scale on the left of the figure. They appear to vary from about 0.1 to 0.3 mm in diameter. Some magnification of the oil globules, along the horizontal axis, occurred in taking the photograph through glass and solvent. Small oil globules are desirable in obtaining a good separation, since the rapidity of attainment of equilibrium is dependent on the surface area.

The circulation of acetone in the extractors was maintained at a rate of about 1.5 ml per minute. If the rate was increased much beyond this value, the smaller globules began to rise and a clogging of the column resulted. The hold-up of the column—i. e., the amount of oil in solution and in the form of globules between flask *B* and oil container *D*—was determined for one of the 6-mm extractors by using a calibrated U-tube instead of the lower reservoir. The height of oil in this tube was noted when the circulation of solvent had first began and again over a period of hours until the level remained constant. From the difference in levels the volume of oil in solution and in the form of globules both in the column and in flask *B* was computed. The volume of oil in flask B was then determined and the difference gave the hold-up of the column. The hold-up, of course, depended on the fractions being investigated, the more soluble fractions giving the greater hold-up. For a distillation cut with kinematic viscosity at 100° F.=0.485 stoke, and using acetone containing 1.5 percent of water as solvent, the hold-up was 11.3 g for a 6-mm column operating at about 27° C. This hold-up would represent about 2 percent of a charge of 500 g.

VIII. DETERMINATION OF PHYSICAL CONSTANTS

Kinematic viscosities at 100 and 210° F. were determined with the aid of the assembly of viscosity pipettes previously described [1]. Where necessary, kinetic energy corrections were applied, and the results are believed accurate to within ±0.5 percent. Viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [4]. Density determinations were made with the aid of the same series of viscosity pipettes, each value recorded being the result of two determinations agreeing within 0.1 percent. Molecular weights were determined by the ebullioscopic method previously described [5], using benzene as a solvent. The results are considered accurate to within ±1 percent, although a precision as high as 0.2 percent was attained in any one determination.

Boiling points at 1 mm of Hg pressure were determined with the aid of a thermocouple calibrated by the Heat Division of this Bureau in an apparatus which has been described previously [6].

Aniline points were determined in the usual manner, with equal volumes of oil and freshly distilled aniline.

Dispersions were obtained from readings on the compensator drum of an Abbe refractometer and the tables provided with the instrument.

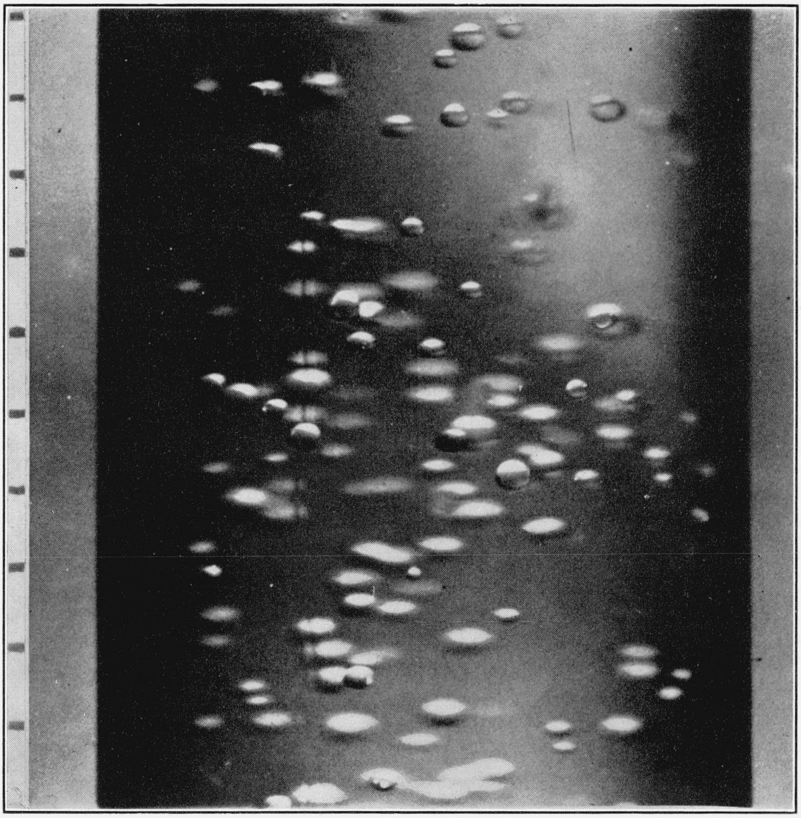

FIGURE 4.—*Small section of the reflux arm of the extractor, showing oil globules.*

The scale at the left is in millimeters.

The optical rotations were measured in a 2-dm tube with a saccharimeter in the Polarimetry Section of this Bureau and converted from °S to $[\alpha]_D$. A precision of about 0.01 in the values of $[\alpha]_D$ was obtained.

The iodine numbers were determined by the Detergents Section of this Bureau (Wijs method). In addition to the petroleum fractions the iodine number of the synthetic hydrocarbon, 1,1-tetralino-*n*-butyl-2-hexadecylethylene, was determined as a check on the accuracy of the iodine-number measurements. This hydrocarbon was kindly furnished by L. A. Mikeska of the Standard Oil Development Co. It should have an iodine number of 58, while the experimentally determined value was 67. Presumably the experimental results are somewhat high, indicating some substitution as well as addition.

IX. DETERMINATION OF CARBON-HYDROGEN RATIOS

The degree of accuracy attained in the combustion analyses is evidenced by the data in table 1 on the combustion of a sample of

TABLE 1.—*Combustion analyses of n-nonacosane* [1]

Weight of sample	Combustion analyses	
	Ratio: $\frac{\text{moles } H_2O}{\text{moles } CO_2}$	Mass sample less mass C+H
g		g/g
0.5215	1.0343	0.0012
0.5074	1.0345	.0008
0.5157	1.0342	.0009
Theoretical ratio	1.0345	

[1] These determinations were made by C. B. Willingham.

n-nonacosane.[4] This high accuracy was made possible by the use of (a) oxygen freed from carbon dioxide, water, hydrogen, and organic impurities in a purification train; (b) a quartz combustion tube containing platinized quartz and copper oxide; (c) the use of hydrogen, in the U-tube adsorbers, as described by Rossini [7], when weighing to minimize errors caused by changes in room temperature and in barometric pressure and to make more certain the change in volume of the solid adsorbents; (d) sealed connections, except for a ground-glass to quartz joint at the inlet end of the combustion tube, and ground-glass joints to attach the U-tube adsorbers to the combustion tube; and (e) a condensation chamber as used by Rossini [8] between the combustion tube and the U-tube adsorbers. This chamber collected temporarily the water and prevented it from condensing on the lubricated ground joints. From this chamber the water was slowly aspirated to the absorber. It was found important to prevent the sample from catching on fire in the platinum boat which contained it, since, when it caught on fire, there was a temporary depletion of the oxygen supply and incomplete combustion resulted, as evidenced by the deposition of carbon at the exit end of the combustion tube. Consequently, the greater part of the sample was aspirated through

[4] This sample was furnished by K. S. Markley, Bureau of Plant Industry, U. S. Department of Agriculture, who prepared it from apple cuticle.

106351—36——8

the tube by slowly moving the small section of the furnace, by means of a thumbscrew, towards and over the sample. Only at the end of the experiment, when burning off carbon, was any flame visible in the boat. The atomic weights used in the computations were 12.009 for carbon and 1.0081 for hydrogen.

X. TABULATION OF RESULTS

Table 2 contains a tabulation of the kinematic viscosities at 100° and 210° F, viscosity indices, and refractive indices for all the fractions from series *A*, *B*, *C*, *D*, *E*, and *F* (see fig. 1), while table 3 records a more complete set of physical properties, together with their empirical formulas, of certain "key" fractions from the same series.

The fact that series *A* is listed in the tables as A_1, A_2, and A_3 requires some explanation. As shown in figure 1, the original charge from which this series was composed was divided into three parts, each of which was extracted separately. By blending the fractions from the three charges according to their physical properties three new charges were prepared, each of which was in turn extracted. It is the fractions from these second charges which are listed in tables 2 and 3 as series A_1, A_2, and A_3.

TABLE 2.—*Physical properties of petroleum fractions*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F	Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F
				SERIES A_1					
%			*Stoke*	*Stoke*	%			*Stoke*	*Stoke*
0.0 to 11.2	1.5032	36	0.6259	0.0655	48.8 to 61.6	1.4836	39	0.6854	0.0695
11.2 to 20.2	1.5025	46	.5441	.0618					
20.2 to 34.7	1.4962	56	.5785	.0656	61.6 to 76.6	1.4778	64	.4887	.0606
34.7 to 48.8	1.4913	35	.7400	.0717	76.6 to 100	1.4701	98	.3078	.0497
				SERIES A_2					
0 to 5.4	1.4836	49	0.5987	0.0658	37.7 to 47.1	1.4717	93	0.3281	0.0511
5.4 to 9.7	1.4780	----	.4516	----	47.1 to 55.5	1.4709	97	.3163	.0504
9.7 to 15.1	1.4781	60	.4538	.0574	55.5 to 63.2	1.4706	97	.3114	.0499
15.1 to 21.1	1.4770	69	.4395	.0576	63.2 to 71.4	1.4704	92	.3016	.0483
21.1 to 28.9	1.4761	74	.4208	.0567					
					71.4 to 83.3	1.4664	110	.2638	.0464
28.9 to 37.7	1.4729	90	.3483	.0526	83.3 to 100	1.4647	123	.2306	.0438
				SERIES A_3					
0 to 6.5	1.4681	117	0.2457	0.0450	50.2 to 59.3	1.4609	136	0.2010	0.0414
6.5 to 11.8	1.4650				59.3 to 67.2	1.4612	134	.2027	.0414
11.8 to 30.3	1.4660	116	.2462	.0450	67.2 to 75.2	1.4607	137	.1977	.0410
30.3 to 41.5	1.4640	125	.2246	.0433	75.2 to 83.2	1.4604	141	.1908	.0404
41.5 to 50.2	1.4613	135	.2020	.0414	83.2 to 100	1.4587	149	.1808	.0398

TABLE 2.—*Physical properties of petroleum fractions*—Continued

SERIES *B*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F
%			*Stoke*	*Stoke*
0 to 6.6	1.4875	70	0.5084	0.0630
6.6 to 12.5	1.4874	72	.4918	.0622
12.5 to 18.4	1.4830	75	.4784	.0615
18.4 to 23.2	1.4805	78	.4560	.0603
23.2 to 25.9	1.4825	73	.4887	.0620
25.9 to 29.3	1.4803	72	.4766	.0614
29.3 to 32.3	1.4797	79	.4641	.0612
32.3 to 35.4	1.4781	78	.4592	.0606
35.4 to 38.5	1.4777	81	.4529	.0605
38.5 to 40.3	1.4775	80	.4537	.0605
40.3 to 42.9	1.4760	85	.4258	.0589
42.9 to 44.8	1.4759	----------	.4240	----------
44.8 to 47.7	1.4749	92	.3857	.0565
47.7 to 49.7	1.4740	93	.3850	.0566
49.7 to 52.2	1.4735	94	.3812	.0564
52.2 to 55.0	1.4736	91	.3885	.0566
55.0 to 57.8	1.4733	92	.3813	.0560
57.8 to 59.5	1.4738	----------	.3949	----------
59.5 to 61.5	1.4728	95	0.3714	0.0556
61.5 to 63.5	1.4730	93	.3780	.0559
63.5 to 65.5	1.4721	96	.3612	.0548
65.5 to 67.8	1.4715	98	.3487	.0539
67.8 to 70.0	1.4702	104	.3242	.0522
70.0 to 72.7	1.4693	108	.3110	.0514
72.7 to 75.0	1.4692	108	.3094	.0512
75.0 to 77.7	1.4685	111	.2962	.0503
77.7 to 80.5	1.4672	116	.2802	.0492
80.5 to 83.2	1.4673	115	.2817	.0491
83.2 to 85.7	1.4670	119	.2762	.0490
85.7 to 87.9	1.4663	120	.2671	.0481
87.9 to 90.6	1.4659	120	.2632	.0476
90.6 to 93.5	1.4652	124	.2543	.0471
93.5 to 95.9	1.4642	128	.2450	.0464
95.9 to 98.4	1.4625	134	.2298	.0452
98.4 to 100	1.4626	----------	----------	----------

SERIES *C*

0 to 5.2	1.4934	60	0.6487	0.0710
5.2 to 9.5	1.4931	58	.6827	.0726
9.5 to 12.9	1.4917	57	.6948	.0733
12.9 to 15.6	1.4889	61	.6751	.0730
15.6 to 17.6	1.4868	61	.6559	.0721
17.6 to 20.1	1.4871	61	.6724	.0729
20.1 to 24.8	1.4855	61	.6698	.0727
24.8 to 26.0	1.4833	63	.6385	.0715
26.0 to 29.0	1.4818	71	.6157	.0710
29.0 to 31.2	1.4811	74	.6031	.0704
31.2 to 33.3	1.4798	72	.5866	.0692
33.3 to 35.2	1.4798		.6063	
35.2 to 36.9	1.4798	----------	.6188	----------
36.9 to 39.0	1.4794	69	.6174	.0707
39.0 to 42.5	1.4787	81	.5857	.0712
42.5 to 44.6	1.4761	81	.5209	.0660
44.6 to 47.8	1.4736	90	.4475	.0618
47.8 to 51.8	1.4728	94	0.4315	0.0610
51.8 to 54.7	1.4725	94	.4261	.0605
54.7 to 57.6	1.4722	95	.4195	.0601
57.6 to 62.6	1.4713	99	.3980	.0589
62.6 to 65.9	1.4703	103	.3780	.0576
65.9 to 69.6	1.4695	104	.3657	.0565
69.6 to 72.3	1.4695	104	.3669	.0568
72.3 to 76.0	1.4689	107	.3513	.0556
76.0 to 79.2	1.4682	111	.3383	.0550
79.2 to 82.1	1.4672	114	.3221	.0536
82.1 to 86.8	1.4668	117	.3135	.0532
86.8 to 88.1	1.4660	119	.3036	.0524
88.1 to 91.1	1.4651	124	.2858	.0510
91.1 to 93.8	1.4637	134	.2730	.0513
93.8 to 100	1.4620	(123)	.2545	.0473

SERIES *D*

0 to 4.6	1.5002	45	1.054	0.0919
4.6 to 8.7	1.5025	46	1.107	.0935
8.7 to 12.5	1.4987	49	1.077	.0928
12.5 to 16.6	1.4928	61	.9067	.0871
16.6 to 20.1	1.4931	56	.9912	.0904
20.1 to 23.1	1.4915	58	.9809	.0904
23.1 to 25.5	1.4882	62	.9273	.0886
25.5 to 27.6	1.4882	61	1.011	.0931
27.6 to 29.8	1.4852	68	.9121	.0895
29.8 to 31.9	1.4847	66	.9179	.0891
31.9 to 33.9	1.4857	62	1.009	.0932
33.9 to 36.0	1.4835	70	.8826	.0883
36.0 to 38.0	1.4796	80	.7471	.0824
38.0 to 40.0	1.4789	80	.7288	.0813
40.0 to 42.0	1.4768	89	.6331	.0769
42.0 to 44.2	1.4771	87	.6581	.0781
44.2 to 48.4	1.4762	90	.6300	.0767
48.4 to 50.5	1.4753	93	0.5893	0.0745
50.5 to 53.2	1.4742	95	.5633	.0729
53.2 to 55.8	1.4734	99	.5347	.0714
55.8 to 58.4	1.4733	100	.5285	.0710
58.4 to 61.0	1.4719	105	.4842	.0684
61.0 to 63.8	1.4719	104	.4891	.0686
63.8 to 66.2	1.4720	102	.4985	.0690
66.2 to 68.7	1.4721	104	.4994	.0694
68.7 to 70.8	1.4716	103	.4827	.0682
70.8 to 73.8	1.4697	112	.4279	.0648
73.8 to 78.5	1.4693	115	.4087	.0633
78.5 to 81.5	1.4692	124	.4137	.0639
81.5 to 86.9	1.4689	117	.4045	.0634
86.9 to 88.2	1.4676	121	.3832	.0620
88.2 to 91.0	1.4670	122	.3726	.0611
91.0 to 93.9	1.4658	128	.3452	.0592
93.9 to 100	1.4643	135	.3193	.0577

TABLE 2.—*Physical properties of petroleum fractions*—Continued

SERIES *E*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F	Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F
%			Stoke	Stoke	%			Stoke	Stoke
0 to 2.9	1.4970	60	1.293	0.1073	52.9 to 55.0	1.4752	99	0.6814	0.0838
2.9 to 6.8	1.4994	55	1.370	.1094	55.0 to 57.0	1.4750	99	.6899	.0844
6.8 to 10.2	1.4999	55	1.380	.1097	57.0 to 58.7	1.4747	100	.6789	.0840
10.2 to 13.6	1.4926	66	1.148	.1023	58.7 to 60.9	1.4746	100	.6796	.0842
13.6 to 16.2	1.4890	76	1.040	.0997	60.9 to 62.8	1.4745	100	.6729	.0834
16.2 to 19.3	1.4856	81	.9322	.0953	62.8 to 65.8	1.4737	103	.6528	.0829
19.3 to 21.7	1.4848	87	.9090	.0959	65.8 to 67.8	1.4736	102	.6530	.0826
21.7 to 24.0	1.4828	86	.8629	.0924	67.8 to 69.5	1.4733	----------	.6443	----------
24.0 to 27.3	1.4828	84	.8893	.0939	69.5 to 71.5	1.4730	104	.6291	.0814
27.3 to 30.0	1.4819	87	.8513	.0921	71.5 to 73.6	1.4730	104	.6318	.0815
30.0 to 32.5	1.4810	87	.8383	.0913	73.6 to 75.3	1.4728	----------	.6237	----------
32.5 to 34.9	1.4802	89	.8209	.0905	75.3 to 77.2	1.4724	107	.6112	.0806
34.9 to 37.0	1.4795	90	.8066	.0901	77.2 to 84.8	1.4721	106	.6107	.0802
37.0 to 39.0	1.4786	94	.7753	.0892	84.8 to 87.3	1.4714	110	.5794	.0789
39.0 to 40.7	1.4778	----------	.7569	----------	87.3 to 89.8	1.4713	109	.5835	.0790
40.7 to 43.2	1.4777	96	.7605	.0889					
43.2 to 45.4	1.4767	96	.7305	.0865	89.8 to 92.0	1.4711	113	.5535	.0773
45.4 to 47.2	1.4760	97	.7095	.0855	92.0 to 94.4	1.4701	113	.5419	.0765
47.2 to 49.1	1.4762	97	.7203	.0862	94.4 to 97.7	1.4692	118	.5204	.0762
49.1 to 52.9	1.4758	98	.7037	.0853	97.7 to 100	1.4690	121	.5303	.0782

SERIES *F*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F	Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at— 100° F	Kinematic viscosity at— 210° F
0 to 4.4	1.4923	75	1.564	0.1280	46.4 to 49.4	1.4791	----------	1.154	----------
4.4 to 9.3	1.4932	74	1.636	.1310	49.4 to 52.9	1.4785	----------	1.106	----------
9.3 to 14.4	1.4917	76	1.554	.1282	52.9 to 56.4	1.4774	94	1.047	0.1084
14.4 to 19.0	1.4898	78	1.477	.1253	56.4 to 62.4	1.4771	94	1.042	.1077
19.0 to 22.8	1.4898	78	1.492	.1259	62.4 to 65.3	1.4762	----------	.9944	----------
					65.3 to 71.0	1.4761	97	.9765	.1053
22.8 to 27.6	1.4891	82	1.442	.1256	71.0 to 75.3	1.4750	100	.9286	.1030
27.6 to 35.3	1.4867	82	1.385	.1224	75.3 to 81.5	1.4745	98	.9259	.1019
35.3 to 39.0	1.4834	83	1.290	.1178	81.5 to 84.4	1.4740	----------	----------	----------
39.0 to 42.8	1.4821	86	1.241	.1166	84.4 to 89.7	1.4728	105	.8280	.0982
42.8 to 46.4	1.4819	87	1.216	.1155	89.7 to 100	1.4714	115	.7332	.0948

TABLE 3.—*Physical properties of "key" fractions*

Series	Fraction	Charge	Molecular weight	Combustion analyses: Ratio moles H_2O/CO_2	Combustion analyses: Mass sample less mass C+H	In the formula $C_nH_{2n}+x$: n	x	Density at— 100° F.	Density at— 210° F.	Density at 77° F. (25° C.) (extrapolated)	Kinematic viscosity at— 100° F.	Kinematic viscosity at— 210° F.	Kinematic viscosity index	Refractive index N_D^{25}	Specific rotation $[\alpha]_D$ at 100° F. (dextro)	Boiling points at 1 mm of Hg.	Dispersion N_F-N_C at 25° C.	Aniline points
		%			g/g			g/ml	g/ml	g/ml	Stoke	Stoke				° C.		° C.
A_1	1 [a]	0.0 to 11.2	[d] (380)	0.8359	0.0114	27.5	−9.0	----	----		0.6259	0.0655	36	1.5032	----	----	----	51.6
	3 [b]	20.2 to 34.7	380.6	.8689	.0024	27.6	−7.2	0.8920	0.8508	0.9006	.5785	.0656	56	1.4962	1.85	204	0.0104	71.6
	6	61.6 to 76.6	385.8	.9490	.0006	27.7	−2.8	.8657	.8257	.8741	.4887	.0606	64	1.4778	1.96	204	.0087	104.1
A_2	7	37.7 to 47.1	385.5	.9664	.0005	27.6	−1.86	.8516	.8119	.8600	.3281	.0511	93	1.4717	1.10	204.5	.0086	107.2
	Residue	83.3 to 100	385.2	.9838	.0019	27.5	−0.89	.8342	.7941	.8426	.2306	.0438	123	1.4647	.31	205.6	----	----
A_3	6 [b]	50.2 to 59.3	386.6	.9941	.0005	27.6	−0.32	.8259	.7857	.8343	.2010	.0414	136	1.4609	.11	208.2	.0083	109.7
	9	75.2 to 83.2	----	----	----	----	----	.8227	.7819	.8312	.1908	.0404	141	1.4604	.05	----	.0084	112.2
	Residue [c]	83.2 to 100	392.4	1.0059	.0003	28.0	+0.35	.8193	.7782	.8278	.1808	.0398	149	1.4587	----	206.3	.0083	113.3
B	1	.0 to 6.6	395.4	.9046	.0032	28.5	−5.4	.8766	.8357	.8851	.5084	.0630	70	1.4875	1.34	212.4	----	----
	7	29.3 to 32.3	398.2	.9382	.0000	28.6	−3.54	.8655	.8247	.8740	.4641	.0612	79	1.4797	1.79	211.5	----	----
	21	63.5 to 65.5	401.0	.9688	.0000	28.7	−1.80	----	----	----	.3612	.0548	96	1.4721	1.22	----	----	----
	34	95.9 to 98.4	406.4	.9943	.0000	29.0	−0.34	.8274	.7880	.8357	.2298	.0452	134	1.4625	.21	217.5	----	----
C	1 [b]	.0 to 5.2	400.2	.8822	.0036	29.0	−6.8	.8866	.8464	.8950	.6487	.0710	60	1.4934	1.20	218.0	.0104	81.9
	15	39.0 to 42.5	412.9	.9493	.0006	29.6	−3.02	.8657	.8260	.8740	.5857	.0712	81	1.4787	1.79	219.4	.0087	106.5
	23 [b]	65.9 to 69.6	417.2	.9737	.0005	29.9	−1.58	.8470	.8060	.8556	.3657	.0565	104	1.4695	.82	222.7	.0085	112.1
	Residue	93.8 to 100	424	.9956	.0002	30.2	−0.27	.8279	.7873	.8364	.2545	.0472	(123)	1.4620	.11	226.1	.0082	116.4
D	2	4.6 to 8.7	421	.8523	.0043	30.5	−9.0	.9000	.8599	.9084	1.107	.0935	46	1.5025	1.06	231.2	.0116	53.7
	17	44.2 to 48.4	444	.9585	.0007	31.8	−2.60	.8597	.8204	.8679	.6300	.0767	90	1.4762	1.22	232.7	.0087	111.4
	30	81.5 to 86.9	451.5	.9796	.0021	32.2	−1.31	.8420	.8009	.8504	.4045	.0634	117	1.4689	.31	235.9	.0087	114.9
	Residue	93.9 to 100	458.6	.9949	.0000	32.7	−0.33	.8299	.7897	.8383	.3193	.0577	135	1.4643	.04	240.7	.0083	121.3
E	3	6.8 to 10.2	431.3	.8677	.0035	31.2	−8.3	.8948	.8553	.9031	1.380	.1097	55	1.4999	.90	245.4	.0107	81.9
	9	24.0 to 27.3	452	.9266	.0008	32.5	−4.8	.8704	.8305	.8788	.8893	.0939	84	1.4828	.87	249.4	.0092	105.1
	20	49.1 to 52.9	477	.9598	.0002	34.2	−2.75	.8569	.8179	.8651	.7037	.0853	98	1.4758	.67	246.4	.0086	115.3
	33	77.2 to 84.8	481.7	.9741	.0015	34.4	−1.78	.8503	.8106	.8587	.6107	.0802	106	1.4721	.39	250.4	.0086	117.5
	Residue	97.7 to 100	495.3	.9820	.0002	35.4	−1.27	.8415	.8018	.8499	.5303	.0782	121	1.4690	.06	260.0	.0084	122.3
F	1	.0 to 4.4	511	.9011	.0040	36.8	−7.4	.8827	.8432	.8910	1.564	.1280	75	1.4923	.45	269.5	.0098	101.1
	7	27.6 to 35.3	519	.9199	.0009	37.4	−6.0	.8747	.8362	.8828	1.385	.1224	82	1.4867	.51	269.5	.0096	107.4
	16	65.3 to 71.0	523	.9598	.0004	37.5	−3.02	.8573	.8180	.8655	.9765	.1053	97	1.4761	.30	271.7	.0086	120.7
	20	84.4 to 89.7	525	.9721	.0010	37.6	−2.10	.8513	.8130	.8591	.8280	.0982	105	1.4728	.09	273.5	.0085	123.0
	Residue	89.7 to 100	537	.9747	−.0003	38.4	−1.95	.8464	.8075	.8545	.7332	.0948	115	1.4714	.00	275.6	.0085	125.2

[a] This fraction was analyzed for sulfur by C. E. Waters of this Bureau, who found it contained 0.08% of S. It was also analyzed for nitrogen and found to contain none, by R. T. Milner of the Bureau of Fixed Nitrogen, U. S. Department of Agriculture. The loss found in the combustion analysis is, therefore, attributable principally to oxygen.

[b] Iodine numbers were determined on these fractions by the Detergents Section of this Bureau. For fractions $A_1$3, $A_3$6, *C*1, and *C*23, the iodine numbers were 21.4, 0.96, 18.1, and 1.9, respectively.

[c] The residues from the extraction all contained small quantities of wax. The wax from fraction A_3 residue was removed by filtration. It had a refractive index N_D^{80}=1.429 and melting point=58° C. This crystalline material appears to be a mixture of normal paraffin hydrocarbons which had escaped removal in the original dewaxing process.

[d] Estimated value, fraction lost.

The percentage of the charge represented by each of the fractions was calculated, not on the basis of the oil charged into the extractors, but on the basis of the total weight of the fractions recovered. The weight of the oil recovered agreed with that charged into the extractor within a few grams, except for series D, where a break in the extractor caused a loss of 163 g.

XI. CONCLUSION

An examination of the physical constants of the oil fractions for series A_1, A_2, and A_3, shows that an excellent separation with respect to type of molecule has been obtained. The kinematic viscosities at 100° F vary from 74 to 18 centistokes, viscosity indices from 35 to 149, refractive indices from 1.5032 to 1.4587, the value of x in the equation C_nH_{2n+x} from -9 to $+0.35$, while the number of carbon atoms to the molecule remains substantially constant. The separation for the charges of higher molecular weight is not quite so satisfactory, and some separation with respect to molecular weight, as well as with respect to type of molecule, is evident. This is probably due to the fact that these higher boiling fractions still had somewhat of a boiling range, as indicated in figure 2.

The authors express their gratitude for the advice and encouragement of F. D. Rossini during this investigation. They also express their gratitude for the advice of M. R. Fenske, of Pennsylvania State College, whose suggestion of the type of extractor column used in this investigation proved valuable.

XII. REFERENCES

[1] B. J. Mair, S. T. Schicktanz, and F. W. Rose, Jr., J. Research NBS **15**, 557–573 (1935) RP849.
[2] R. N. J. Saal and W. J. D. Van Dyck, Proc. World Petroleum Congress, London, Proc. 2, 352–358 (1933).
[3] M. R. Cannon and M. R. Fenske, Ind. Eng. Chem. **28**, 1035 (1936).
[4] R. E. Hersh, E. K. Fisher, and M. R. Fenske, Ind. Eng. Chem. **27**, 1441–6 (1935).
[5] B. J. Mair, J. Research NBS **14**, 345–357 (1935) RP772.
[6] S. T. Schicktanz, J. Research NBS **14**, 685–692 (1935) RP796.
[7] F. D. Rossini, BS J. Research **6**, 7 (1931) RP259; J. Research NBS **6**, 39 (1931) RP260.
[8] F. D. Rossini, BS J. Research **8**, 121 (1932) RP405.

WASHINGTON, September 2, 1936.